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Fenton pre-treatment of wastewater containing nitrobenzene using ORP for indicating the endpoint of reaction

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Abstract

Because of their high toxicity and refractory to microorganisms, high concentration aromatic compounds like nitrobenzene (NB) have long been considered to be disadvantageous to stable operation of biological wastewater treatment systems in petrochemical industries. The pre-treatment of NB-bearing dye producing wastewater using Fenton's oxidation was studied with the objective to remove NB and related aromatic compounds, and therefore improve the biodegradability of wastewater. Under the conditions of initial pH=3, H_2O_2=500 mg l^{-1}, H_2O_2/Fe^{2+} (in weight) =6, and reaction time =150 min, the BOD/COD ratio of wastewater was increased from 0.03 to 0.47. The redox potential (ORP) was found to be an effective indicator to monitor the Fenton's oxidation process. H_2O_2 was almost depleted at the point where the ORP reached the maximal value, and the lowest point of ORP was accompanied with the completion of Fenton's oxidation and the maximal BOD/COD. Increase of biodegradability continued for about 60 min even after the depletion of H_2O_2, suggesting the existence of some unknown oxidizing species.

Keywords: Fenton's oxidation; dye producing wastewater; nitrobenzene; redox potential; biodegradability

1. Introduction

Microorganisms must be domesticated for a long period to degrade NB and other aromatic compounds[1,2]. So for some chemical industries which discontinuously discharge NB-bearing wastewater, it is difficult to keep a stable biological wastewater treatment. In such cases, it is necessary to destruct the structures of the refractory aromatic compounds in wastewater and improve the biodegradability of wastewater to guarantee the stability of biological systems and the quality of treated effluents. Mu et al. used zero-valent iron as a pretreatment method to reduce NB to aniline which could be degraded by microorganisms under aerobic conditions[3]. Various chemical oxidation technologies, such as ozonation[4], supercritical oxidation[5], photo-catalysis[6], and photo-assisted Fenton's oxidation[7], etc., have also been utilized for the removal of NB. However, these methods are impractical either because of the difficulty in operation or high costs. In comparison, Fenton's oxidation has been widely applied for the treatment or pretreatment of refractory wastewater because of its reasonable cost performance and ease of operation[9-12]. Under acidic conditions, catalytic decomposition of H_2O_2 by Fe^{2+} induces a free radical chain reaction

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process. The hydroxyl radicals produced, which possess high oxidation ability, decompose refractory organics into biodegradable compounds in a short time[13,14]. However, how to control Fenton's oxidation to achieve the maximum improvement of wastewater biodegradability still remains to be unclear until now.

In this study, Fenton's oxidation was used as a pretreatment technology to improve biodegradability of the NB-bearing refractory waste stream from a dye producing factory. The effects of Fenton's reagent dosage, the ratio of H_2O_2 to Fe^{2+}, and reaction time on the removal of NB and the improvement of the biodegradability of wastewater were investigated, and the possibility of using redox potential (ORP) as an indicator for judging the endpoint of reaction was evaluated.

2. Materials and methods

2.1 Materials

Wastewater samples were taken from a dye manufacturing plant which uses nitrobenzene as one of the main raw materials. The characteristics of wastewater are shown in Table 1. With a BOD to COD ratio as low as <5%, the waste stream demonstrates a very low biodegradability.

H_2O_2 (w/w, 30%), $FeSO_4 \cdot 7H_2O$, and NaOH of analytical grade were purchased from the Sigma Chemical Company (USA).

Table 1. Average composition of the dye producing wastewater

COD (mg l^{-1})	BOD (mg l^{-1})	TOC (mg l^{-1})	NB (mg l^{-1})	TSS (mg l^{-1})	pH
1300	54	413	115	92	1.8-2.1

2.2 Fenton's oxidation

Fenton's oxidation was carried out without temperature control as follows:

- 500 ml wastewater sample was added in a beaker, followed by adjusting the pH to 3.03±0.1 with NaOH [8,15].
- The scheduled Fe^{2+} dosage was achieved by adding necessary amount of solid $FeSO_4 \cdot 7H_2O$.
- A given volume of 30% (w/w) H_2O_2 solution was added to start up the Fenton's reaction.
- After reaction for a given time, the pH of the solution was adjusted to 8.0±0.1 by adding sodium hydroxide under agitation to precipitate residual ferric ions. Agitation was continued under the above pH for 30 min.
- After sedimentation for 60 min, the supernatant was taken for analysis.

All of the experiments were performed in triplicate.

2.3 Analysis

TOC (total organic carbon) analysis was performed on a TOC analyzer (Phoenix, 8000, Tekmar-Dohrmann Co., USA). The concentration of H_2O_2 was determined by iodometric method. ORP was measured with a portable metre (TOA, Japan). COD (chemical oxygen demand), BOD (biochemical oxygen demand) and TSS (total suspended solids) were measured according to the *standard methods* [16]. The COD content in the treated effluents was calculated by subtracting the COD contributed by the residual H_2O_2 from the total COD [17]. The BOD was measured after the sample's pH was adjusted to 8.0 by adding NaOH.

Electron spin resonance (ESR) measurements were conducted on a Bruker Elexsys Spectrometer (ESP, 300E) at 9.80 GHz and room temperature. The ESR settings were: modulation frequency, 100 kHz; microwave power, 20 mW; and sweep width, 100.0 G.

All the analyses except for ESR were carried out following filtration by a 0.45 μm membrane filter. For ESR measurements, samples were quickly taken without filtration from the reaction system during the Fenton's oxidation and applied for analyses immediately

3. Results and discussion

3.1 The effect of H_2O_2/Fe^{2+} ratio on Fenton's oxidation

To establish a suitable H_2O_2/Fe^{2+} ratio for the treatment of the NB-bearing wastewater, the dose of Fe^{2+} was changed under an H_2O_2 concentration of 1500 mg l^{-1}. The reaction time was 2 h.

Figure 1a shows variations of residual H_2O_2 concentration and ORP under different Fe^{2+} doses, and Fig. 1b shows variations of COD and TOC. The residual H_2O_2 decreased quickly with the increase of Fe^{2+} dose, and there was almost no residual H_2O_2 existed under an Fe^{2+} dose of 250 mg l^{-1}, corresponding to the H_2O_2/Fe^{2+} ratio of 6:1. On the other hand, the ORP increased with the increase of Fe^{2+} dose, reaching the maximal value of 475 mV at the Fe^{2+} dose of 250 mg l^{-1}.

Then, the ORP decreased gradually with the further increase of Fe^{2+} dose. When there is enough H_2O_2 in the system, Fe^{2+} will soon be oxidized to Fe^{3+} after addition. When Fe^{2+} is over dosed, residual Fe^{2+} began to occur in the system, and the residual Fe^{2+} concentration will increase with the increase of Fe^{2+} dose. Therefore, the maximal value of ORP is the point where there is neither residual H_2O_2 nor Fe^{2+} existing in the system [18].

As shown in Fig. 1b, the COD removal increased quickly with the increase of Fe^{2+} dose at first. However, when the Fe^{2+} dose was over 250 mg l^{-1}, the COD removal began to decrease slowly with the increase of Fe^{2+} dose. Although Yoon et al. indicated the possibility of the consumption of hydroxyl radicals by the residual Fe^{2+} [19], the fact that the TOC removal did not decrease even under an Fe^{2+} dose as high as 1500 mg l^{-1} suggests that the consumption of hydroxyl radicals by the overdosed Fe^{2+} might not be a serious problem in this case. So the possible reason for the decreased COD removal might be the contribution of COD by the residual Fe^{2+}. The TOC removal, on the other hand, indicates a different trend: it increased quickly to over 20% at an Fe^{2+} dose of 100 mg l^{-1}, and then increased slowly with the further increase of Fe^{2+} dose. As shown in Fig. 1b, discrepancy between the TOC and COD removal trends appeared when the Fe^{2+} dose was increased from 100 mg l^{-1} to 250 mg l^{-1}. This discrepancy might be attributed to the partial oxidation of organic compounds[20]. Since partial oxidation is favorable for improving the biodegradability of wastewater, a weight ratio of H_2O_2/Fe^{2+} of 6 was selected for Fenton's pretreatment based on the above results.

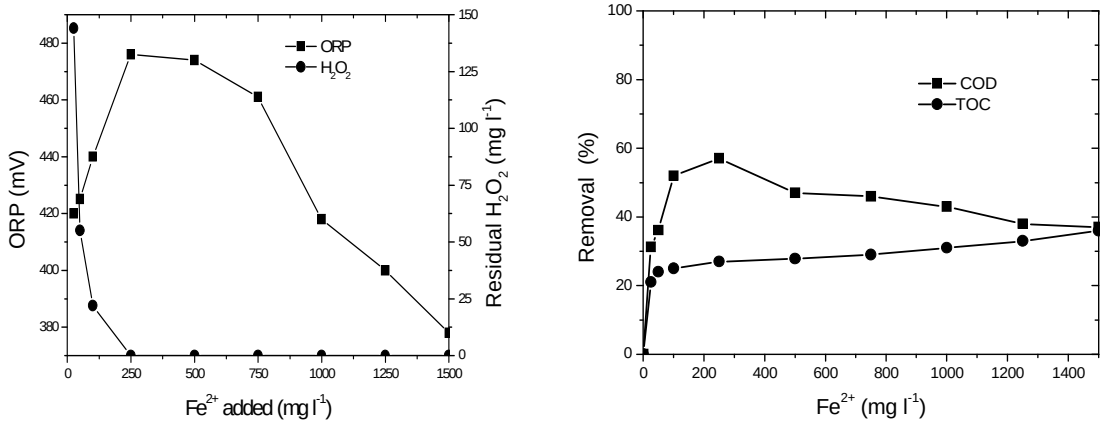

Fig.1. (a) Effect of Fe^{2+} dosage on the variations of ORP and residual H_2O_2; (b) Effect of Fe^{2+} dosage on the removals of COD and TOC

3.2 Effect of H_2O_2 and Fe^{2+} doses on Fenton's oxidation

The effects of Fenton's reagent dose on COD removal and the BOD/COD ratio were investigated at the weight ratio of H_2O_2/Fe^{2+} of 6, and the results are shown in Fig. 2a and Fig. 2b. As shown in Fig. 2a, both the values of COD before and after neutralization-sedimentation, which indicates the COD removal performance by oxidation and by the combination of oxidation and adsorption, respectively, increased with the increase of the Fenton's reagent dose. It is clear that the adsorption by ferric hydroxide formed during neutralization contributed much to the COD removal when the H_2O_2 dose was 500 mg l^{-1} (corresponding Fe^{2+} dose, 84 mg l^{-1}). As for the BOD/COD ratio, there appeared a maximal value of 0.47 at the H_2O_2 dose of 500 mg l^{-1} and corresponding Fe^{2+} dose of 84 mg l^{-1}. With the further increase of the dose, significant decrease of BOD/COD ratio appeared, perhaps due to the mineralization of part of biodegradable organic matters by hydroxyl radicals. Since the main purpose of the pretreatment is to increase the biodegradability of wastewater for the following biological treatment, the suitable dosage of Fenton reagent was determined as H_2O_2 of 500 mg l^{-1} and Fe^{2+} of 84 mg l^{-1}.

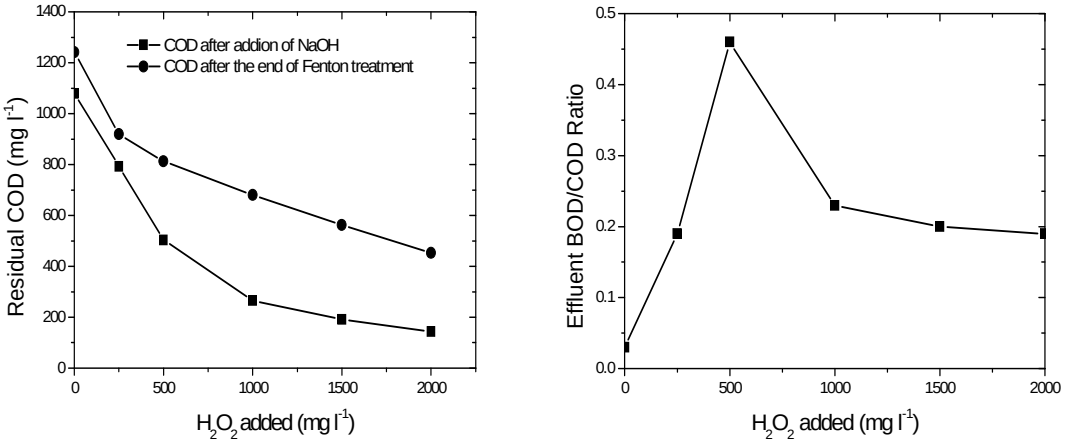

Fig. 2. (a) Effect of the dose of Fenton reagent on COD removal; (b) Effect of the dose of Fenton reagent on the variation of BOD/COD ratio

3.3 Effects of reaction time on Fenton's oxidation

The effects of reaction time on the pretreatment performance were investigated under an H_2O_2 of 500 mg l^{-1} and Fe^{2+} of 84 mg l^{-1}. Variations of BOD/COD ratio and residual COD are shown in Fig. 3a, and variations of H_2O_2 and ORP are shown in Fig. 3b. From Fig. 3a, it can be seen that the decrease of COD became very slow after 90 min reaction. However, the BOD/COD ratio kept increasing until 150 min, indicating that it is beneficial for the improvement of the biodegradability of wastewater by extending the reaction time to 150 min.

On the other hand, Fig. 3b shows that there existed two turning points of ORP during the reaction: the beginning of fast decrease of ORP at 90 min and the stop of the fast decrease of ORP at 150 min. The first turning point of ORP appeared in accordance with the disappearance of residual H_2O_2, indicating that the residual H_2O_2 concentration might be a key factor in controlling the value of ORP. Lopez et al. also found similar phenomenon, and designated this point as the endpoint of Fenton's oxidation[21]. However, Fig. 3a indicates that the oxidation reaction did not stop until the ORP reached the second turning point at 150 min, suggesting that there existed oxidizing species in the system between the first and second ORP turning points although H_2O_2 was depleted. So it is clear that in stead of residual H_2O_2, ORP could be used as an important parameter to indicate the end of the oxidizing reaction for pretreatment.

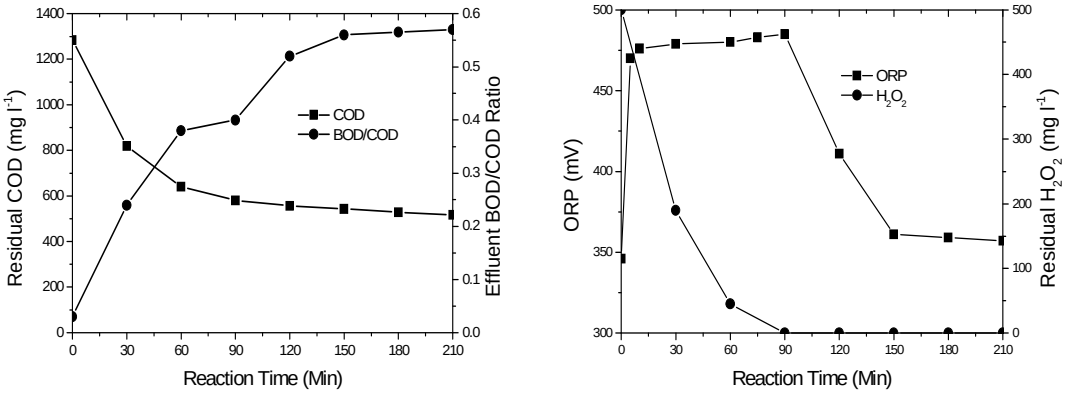

Fig. 3. (a) The variations of COD removal and BOD/COD ratio with reaction time; (b) The variations of ORP and residual H_2O_2 with reaction time

Generally hydroxyl radicals produced by the catalytic decomposition of H_2O_2 are considered to be the main oxidizing species in Fenton's oxidation process. So it is interesting that the oxidation reaction continued for 60 min even after the depletion of H_2O_2, the source for producing hydroxyl radicals. To investigate if the hydroxyl radicals were the main oxidizing species after the depletion of H_2O_2, ESR spectra of hydroxyl radical adducts of 5,5-dimethyl-4,5-dihydro-3H-pyrrole-N-oxide (DMPO) during the Fenton's oxidation were recorded (Fig. 4). It is clear that the hydroxyl radicals could not be produced after the depletion of H_2O_2. Therefore, it is possible that some other oxidizing species, which could transform the organic compounds from the refractory structures to biodegradable structures, existed in the Fenton's system, and these species played an important role in the improvement of biodegradability after the depletion of H_2O_2. However, further studies are required to clarify the mechanisms.

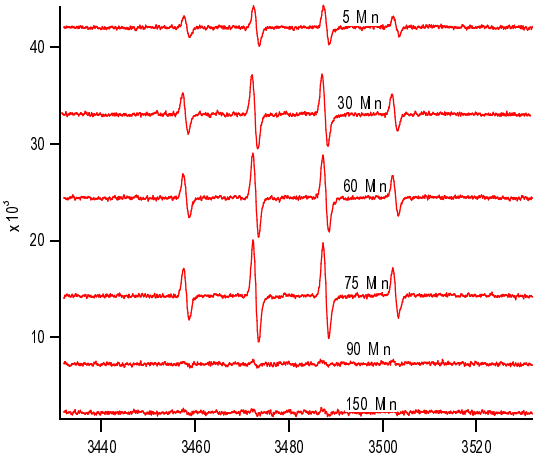

Fig. 4. ESR spectra of hydroxyl radical adducts of DMPO (100mM) in the process of Fenton's oxidation

4. Conclusions

The effectiveness of Fenton's oxidation as a pretreatment method for nitrobenzene bearing dye producing wastewater treatment was investigated with the objective of improving the biodegradability of the wastewater. The following conclusions could be drawn from the study:

- Under the conditions of initial pH=3, H_2O_2=500 mg l^{-1}, H_2O_2/Fe^{2+}=6, and reaction time =150 min, the biodegradability of the dye producing wastewater was greatly improved by Fenton's oxidation. The value of BOD/COD was increased from the initial 0.03 up to 0.47.
- The ORP could be used as a useful indicator to monitor the Fenton's process. The first ORP turning point indicates the depletion of H_2O_2 in the solution, and the second point indicates the end of Fenton's oxidation.
- Oxidation continued for a long time after the depletion of H_2O_2, which might be attributed to the existence of some oxidizing species with an oxidation potential lower than hydroxyl radicals. But further studies are required to clarify the mechanisms.

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